

Kinetics of epoxy-asphalt oxidation

Apostolidis, P.; Liu, X.; Erkens, S.; Scarpas, Athanasios

DOI

[10.1201/9781003027362-92](https://doi.org/10.1201/9781003027362-92)

Publication date

2020

Document Version

Accepted author manuscript

Published in

Advances in Materials and Pavement Performance Prediction II

Citation (APA)

Apostolidis, P., Liu, X., Erkens, S., & Scarpas, A. (2020). Kinetics of epoxy-asphalt oxidation. In A. Kumar, A. T. Papagiannakis, A. Bhasin, & D. Little (Eds.), *Advances in Materials and Pavement Performance Prediction II: Contributions to the 2nd International Conference on Advances in Materials and Pavement Performance Prediction (AM3P 2020), 27-29 May, 2020, San Antonio, Tx, USA* (1 ed., pp. 398-401). Taylor and Francis. <https://doi.org/10.1201/9781003027362-92>

Important note

To cite this publication, please use the final published version (if applicable).
Please check the document version above.

Copyright

Other than for strictly personal use, it is not permitted to download, forward or distribute the text or part of it, without the consent of the author(s) and/or copyright holder(s), unless the work is under an open content license such as Creative Commons.

Takedown policy

Please contact us and provide details if you believe this document breaches copyrights.
We will remove access to the work immediately and investigate your claim.

Kinetics of epoxy-asphalt oxidation

Panos Apostolidis^{1*}, Xueyan Liu¹, Sandra Erkens¹ & Athanasios Scarpas^{2,1}

¹ *Section of Pavement Engineering, Faculty of Civil Engineering and Geosciences, Delft University of Technology, Delft, the Netherlands.*

² *Department of Civil Infrastructure and Environmental Engineering, Khalifa University of Science and Technology, Abu Dhabi, United Arab Emirates.*

ABSTRACT: In-depth understanding of the temperature effect on oxidative aging in epoxy-asphalt blends is needed to enable accurate predictions on material response through their service life. Details of the significance of developing prediction models and tools on oxidative aging of pavement materials are presented in a companion paper (Apostolidis et al., *Oxidation Simulation of Thin Bitumen Film*. AM3P). In this research, the chemical compositional changes of epoxy modified asphalt binders, with and without filler, were analysed after oven-conditioning by means of Fourier transform infrared (FTIR) spectroscopy. With the carbonyl and sulfoxide compounds as aging indices, the sensitivity of chemical compositional changes of bituminous and epoxy-based systems due to the applied temperatures was observed.

1. INTRODUCTION

Nowadays, the asphalt industry has been focused on exploring new binders and modification technologies in an effort to offer a panoply to pavements against the climate change and the continuously increasing traffic volumes. Bitumen is product of petroleum refining process comprising in majority of non-polar, high molecular weight hydrocarbons, and currently it is the most dominant binding material used in pavements. Nevertheless, most asphalt pavements exhibit shortcomings in terms of durability and together with the top priority of road administrations to minimize the regular maintenance and reconstruction operations, super-durable pavement materials are highly demanding.

In this context, long-life pavements have started to attract the interest of road agencies and policy makers all over the world. Pavement structures of enhanced longevity would be expected to reduce the major repair needs justifying their high initial costs. New or relatively new binding systems specially designed to produce durable and long-lasting pavement materials have been proposed. One quite promising technology is the epoxy-based polymers which are able to lower the fracture (Youtcheff et al. 2006, Widyatmoko et al. 2006) and aging sensitivity of asphalt materials (Herrington & Alabaster 2008, Apostolidis et al. 2019b & 2020), and they have been utilized successfully for bridge and road pavements (Lu & Bors 2015, ITF 2017).

In comparison with the thermoplastic block copolymers, epoxy-based polymers are thermo-

hardening materials which cannot be re-melted once they are fully cured (Apostolidis et al. 2018 & 2019a). Previous studies gave special emphasis on assessing the incorporating chemistry of epoxy-based polymers used in bitumen and the way this affects the evolution of physico-mechanical properties of asphalt paving materials under certain energy conditions (Apostolidis et al. 2018 & 2019a). The impact of epoxy-based polymers in bitumen with and without filler on its aging performance was evaluated as well (Apostolidis et al. 2019b & 2020). However, fundamental understanding of oxidation mechanism of epoxy polymers is still needed because of the different nature of epoxy-based polymers comparing the conventional binders.

Especially, quantitative information on the rate of chemical compositional, physical and mechanical changes of epoxy-asphalt materials as function of time is important to predict precisely the evolution of material properties through their service life. Until now, predictions on the long-term performance of epoxy asphalt materials were with single-point data sets on the time scale at 130°C in the lab, much higher than the actual pavement temperatures (Apostolidis et al. 2019b & 2020). Useful lab data with pragmatic implications are missing to simulate the exact aging mechanism of such polymeric materials. Thus, kinetic data are important to assist on more reliable predictions of the long-term pavement performance, and this was the main scope of this research; to provide the kinetics parameters of oxidizing epoxy-modified asphalt materials.

2. MATERIALS AND METHODS

A 70-100 pengrade bitumen was selected for this research. A non-reactive filler passed through the 0.075-mm sieve were used to formulate the studied mastics. The epoxy-asphalt (EA) binder, supplied by ChemCo Systems, is formulated from two liquid parts; (i) the Part A (epoxy resin formed from epichlorhydrin and bisphenol-A) and (ii) Part B (fatty acid hardening agent in 70 pen bitumen). According to the supplier, Part A and B were oven-heated separately for 1 hour, at 85°C and 110°C, respectively. Afterward, Part A and B (weight ratio of 20:80) were mixed together for approximately 10 to 20 seconds, and the EA binder was produced.

Bitumen is always in conjunction with mineral particles (i.e., filler and aggregates) of different sizes in asphalt pavements. Filler particles together with bitumen form the mastic which is the binding system between the aggregates and may act as catalyst or inhibitor through the bitumen oxidation process, a possibility which needs further investigation. Thus, as in (Apostolidis et al. 2020), mastic samples were prepared as well by mixing fillers with the newly formulated binders with 56:44 weight ratio. Four mastic samples were studied of different weight ratio of 0:100 (EBF0), 20:80 (EBF20), 50:50 (EBF50) and 100:0 (EBF100) of EA binder and bitumen. To assess the influence of filler on oxidation kinetics of studied materials, the neat bitumen and EA binder were aged as well. All samples were placed in a refrigerator at -10°C to prevent any reaction.

Samples were subjected to oven-conditioning (0.1-MPa) over 0, 2, 5, 8, 24, 120, 240 and 480 hrs lengths of time at 80, 90 and 100°C. After each time period, the chemical compositional changes due to aging were measured as function of time through Fourier Transform Infrared (FT-IR) spectroscopy. IR spectra with wavenumber from 4,000 to 600 cm^{-1} were recorded and collected for all the samples as in (Apostolidis et al. 2019b & 2020). A minimum of three sub-samples were investigated for each sample and 20 scans per sub-sample were performed with a fixed instrument resolution of 4 cm^{-1} . Carbonyl (CO) and sulfoxide (SO) compounds are the typical aging indices which are defined as the integrated peak area from 1753-1660 cm^{-1} and 1047-995 cm^{-1} , respectively. Herein, their values were calculated by using the area method representing the extent of age of neat and epoxy-based systems. The calculation is performed by dividing the area under a specific location of the spectrum by the sum of other specific areas.

3. RESULTS AND DISCUSSION

Conditioning performed in an oven under 0.1 MPa of air pressure at three different temperatures; 80, 90 and 100°C. As mentioned earlier, the ultimate scope was to determine the oxidation reaction kinetic parameters of epoxy-modified asphalt binders and mastics. The evolution of SO and CO in bitumen and EA binders over oven-conditioning at different temperatures is demonstrated in **Fig. 1(a)** and **(b)**, respectively. The total amount of these compounds in the studied binders did not change dramatically at 80°C, however remarkable effect of temperature was noticed with increasing the applied temperature to 100°C. This trend is shown also when filler was added in these binders, see **Fig. 2**.

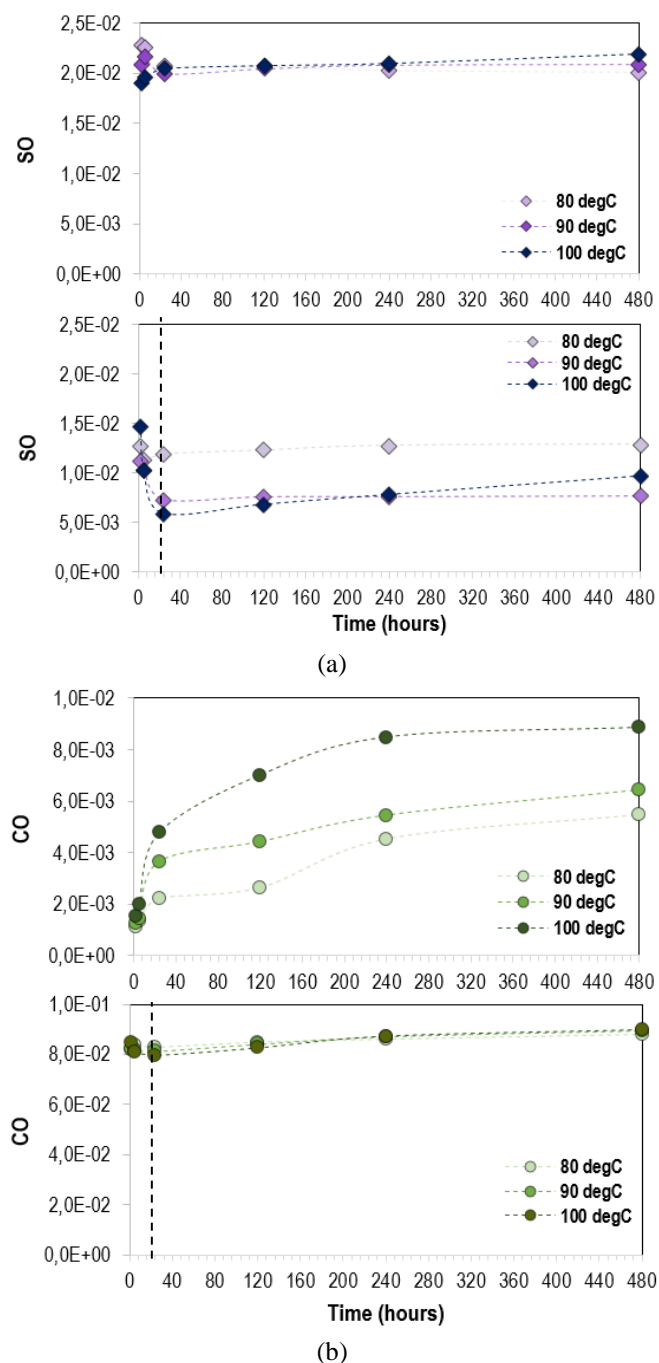


Fig. 1 Change of (a) SO and (b) CO compounds of bitumen (top) and EA binder (bottom) over oven-conditioning at 80, 90 and 100 °C.

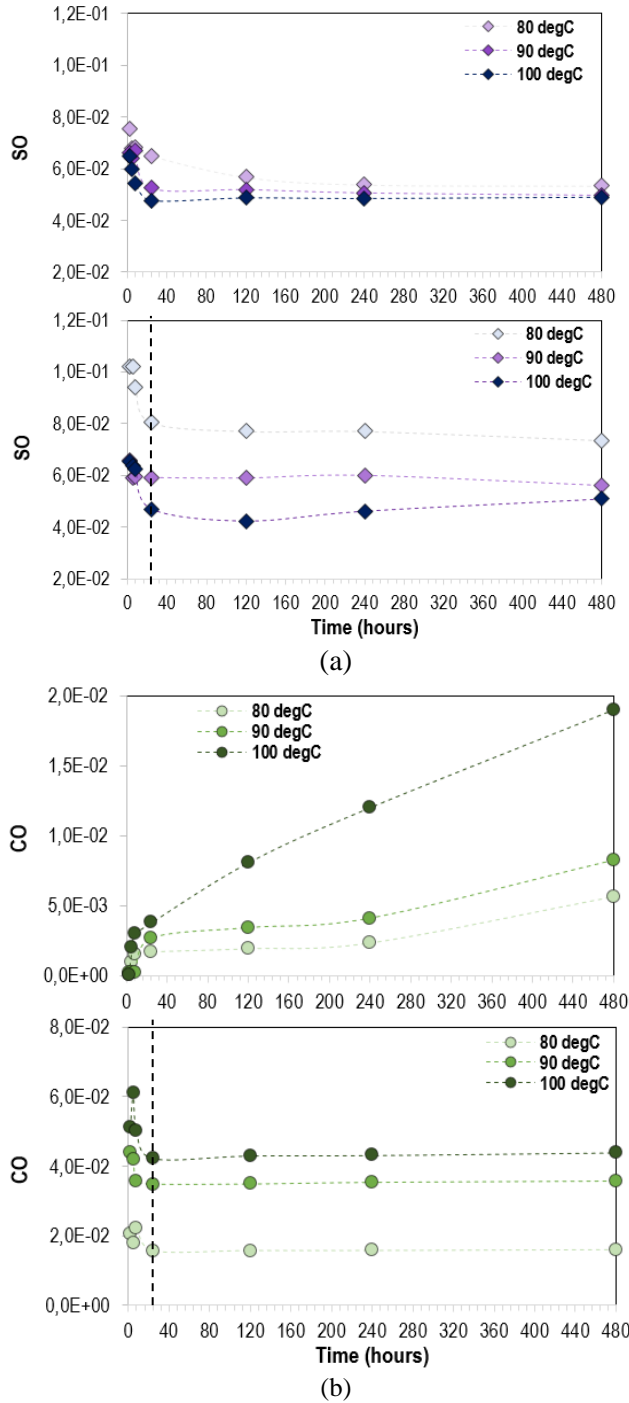


Fig. 2 Change of (a) SO and (b) CO compounds of bituminous (top) and EA mastic (bottom) over oven-conditioning at 80, 90 and 100 °C.

A decreasing trend of CO and SO compounds of EA systems at the early phase of oven-conditioning (first 24 hrs) is shown in **Fig. 2**, possibly due to the epoxy polymerization. The SO compounds of bitumen and bituminous mastic remain almost unchanged through the aging at 80 and 90°C. However, the sulfur reacting species of studied mastics have shown an increasing trend at 100°C, a phenomenon which coincides with the increase attribute of SO in epoxy-modified materials at 130°C (Apostolidis et al. 2019b & 2020).

For quantitative reason, the incremental values of CO compounds, which are not demonstrated herein,

used to determine the kinetic parameters of epoxy asphalt aging. The extent of CO incremental values of EA systems increased more rapidly than of the bituminous materials showing that CO of epoxy-based polymers were more temperature sensitive than of bitumen. Therefore, the activation energy of CO formation in EA systems is expected to be lower than of bituminous ones. Incremental values of CO compounds have been used for the determination of oxidation kinetic parameters, which are provided in the following sub-section.

Oxidation Kinetic Parameters

The chemical reaction of oxidation process in studied materials is expressed as

$$\frac{\partial x}{\partial t} = k(1 - x)^n \quad (1)$$

Thus, the first-order rate expression of reaction kinetics is as

$$\frac{\partial x}{\partial t} = k(1 - x) \quad (2)$$

and by calculating its integral

$$\ln(1 - x) = \ln(1 - x_0) - kt \quad (3)$$

where x is the reacted carbon or carbonyl compounds at different times, k is the reaction rate coefficient, n is the reaction order number, t is the oxidation time, x_0 is the initial carbonyl content.

Because conditioning temperature affects the chemical reactions and the transformation rate of carbon to carbonyl compounds, these effects can be incorporated into the reaction rate coefficients by using the Arrhenius approach as

$$\ln k = \frac{E_a}{RT} + \ln A \quad (4)$$

where E_a is the activation energy, R is the universal gas constant, T is the absolute temperature, k is the reaction rate coefficient, A is the reaction factor.

Based on the data generated by the incremental values of CO in both EA and bituminous materials, **Fig. 3** plots the relationship between $-\ln(k)$ and $1/T$. **Fig. 4** demonstrates the relationship of E_a and A values, which were derived from **Fig. 3**, with epoxy proportion in bitumen obtained from **Eq. 4**. From **Eq. 4** and **3**, the final form of the oxidation kinetic equation of binders becomes as

$$\ln(1 - x) = \ln(1 - x_0) - A e^{\left(\frac{E_a}{RT}\right)} t \quad (5)$$

temperature sensitive and oxygen resistant systems, respectively.

REFERENCES

- Apostolidis, P., et al. 2018. Chemo-rheological study of hardening of epoxy modified bituminous binders with the finite element method. *Transportation Research Record* 2672, pp. 190-199.
- Apostolidis, P., et al. 2019a. Kinetic viscoelasticity of crosslinking epoxy asphalt. *Transportation Research Record* 2673, pp. 551-560.
- Apostolidis, P., et al. 2019b. Evaluation of epoxy modification in bitumen. *Construction and Building Materials* 208, pp. 361-368.
- Apostolidis, P., et al. 2020a. Evaluation of epoxy modification in asphalt mastic. *Construction and Building Materials*.
- Branthaver, J.F., et al. 1993. *Binder characterization and evaluation, Volume 2: Chemistry*. Report SHRP-A-368.
- Herrington, P., & D. Alabaster. 2008. Epoxy modified open-graded porous asphalt. *Road Materials and Pavement Design* 9(3), pp. 481-498.
- Long-life surfacings for roads: Field test results*. 2017. International Transport Forum, OECD, Paris, France.
- Lu, Q., & J. Bors. 2015. Alternate uses of epoxy asphalt on bridge decks and roadways. *Construction and Building Materials* 78, pp. 18-25.
- Petersen, J.C., et al. 1993. Effects of physicochemical factors on asphalt oxidation kinetics. *Transportation Research Record* 1391, pp. 1-10.
- Petersen, J.C., & P.M. Harnsberger. 1998. Asphalt aging: Dual oxidation mechanism and its interrelationships with asphalt composition and oxidative age hardening. *Transportation Research Record* 1638, pp. 47-55.
- Widyatmoko, I., et al. 2006. Curing characteristics and the performance of epoxy asphalts. *Proceedings of the Canadian Technical Asphalt Association* 51.
- Youtcheff, J., et al. 2006. The evaluation of epoxy asphalt and epoxy asphalt mixtures. *Proceedings of the Canadian Technical Asphalt Association* 51.

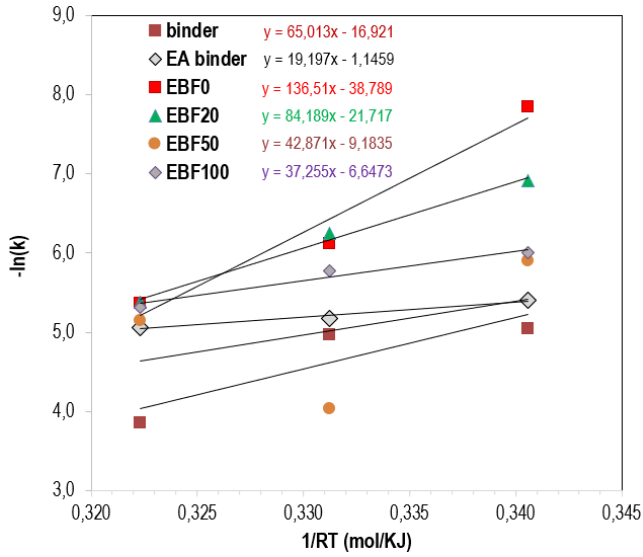


Fig. 3 $-\ln(k)$ versus $1/RT$ through oven-conditioning for the studied (a) binders and (b) mastics.

Table 1 Kinetic parameters of studied materials.

Percentage of EA	A (1/hrs)	E_a (KJ/mol)
<i>without filler</i>		
0	2,23E+07	65,013
100	3,15E+00	19,197
<i>with filler</i>		
0	7,01E+16	136,510
20	2,70E+09	84,189
50	9,74E+03	42,871
100	7,71E+02	37,255

All studied materials indicate similar curve-fitting results (**Fig. 3**) and the values of Arrhenius coefficients (i.e., activation energy and reaction rate) were calculated and provided in **Table 1**. In **Fig. 3**, the reaction rates of all materials illustrate a reasonably fit to the Arrhenius temperature dependency. Further, the temperature sensitivity of materials is represented by the values of activation energy. As indicated in previous studies (Branthaver et al. 1993, Petersen et al. 1996, Petersen & Harnsberger 1998), the activation energy of CO development in bitumen is generally higher than of SO. So, the CO formation is less temperature sensitive than of SO. Hence, the low values of activation energy of epoxy modified mastics correspond to more temperature sensitive systems comparing the unmodified bituminous materials. Increase of activation energy of bitumen and epoxy-modified binders with filler was noticed in **Table 1**. Thus, decrease of overall oxidation sensitivity is indicated with the addition of filler at any given temperature. Overall, the increase of epoxy proportion in bitumen, with and without filler, leads to decrease of activation energy and reaction rate of CO formation, and thus to